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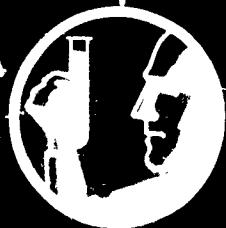
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THE DEVELOPMENT OF HIGH-RELIABILITY PAINTS FOR AIRCRAFT

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THE DEVELOPMENT OF HEAT-RESISTANT PAINTS FOR METALS

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TABLE OF CONTENTS

	Page
ABSTRACT	
I. INTRODUCTION	1
II. SUMMARY	2
III. MATERIALS AND PROCEDURES	3
A. Materials	3
B. Coating Evaluation Procedures	3
IV. EXPERIMENTAL RESULTS AND DISCUSSION	5
A. Studies of Reactions of ZnO with Phosphates	5
1. Reaction of zinc oxide with polyphosphoric acid or polyphosphoric esters	5
a. Preparation of esters	5
b. Reactions with polyphosphoric acid	6
c. Reactions with esters of polyphosphoric acid	6
2. Reaction of zinc oxide with d-n-butylamine phosphate.....	7
B. Studies of the ZnO-DMHP Reaction	8
1. Effects of temperature and relative humidity during curing	8
a. ZnO-DMHP-EAP coatings	8
b. ZnO-DMHP-Ludox coatings	11
2. Effects of curing time.....	13
a. Weight loss during curing	13
b. Curing time at 72°F and 75% RH	15
3. Condition of substrate	15
C. Studies of the Weatherability of ZnO-DMHP-EAP Coating	17
V. FUTURE WORK	17
ACKNOWLEDGMENTS	18
DISTRIBUTION LIST	19

ABSTRACT

Products formed by the reaction of zinc oxide with polyphosphoric acid or esters of polyphosphoric acid are similar in some respects to the products of the reaction of zinc oxide with dimethyl hydrogen phosphite (DMHP). This similarity indicates that the reaction with DMHP may proceed through a step involving formation of polyphosphate intermediates.

Experiments with zinc oxide and di-n-butylamine phosphate resulted in the preparation of heat-resistant coatings, but the coatings were not water resistant.

Coatings that were hard, well bonded, heat resistant, and water resistant were produced repeatedly from a mixture of ZnO, DMHP, and a dispersion of colloidal silica when they were cured at 72°F and 75% RH; when cured at 70% or 80% RH, the coatings were not heat resistant. The properties of ZnO-DMHP-EAP coatings cured at 72°F and various relative humidities varied erratically, and in no case was a coating obtained that was both water resistant and heat resistant.

Coatings of mixtures of ZnO-DMHP and colloidal silica reach constant weight in less than 2 hours when cured in air at normal temperatures. The weight loss corresponds fairly closely to that calculated for the loss of all methyl groups in DMHP and the water in the silica dispersion.

Comparison of several methods of pretreatment of aluminum panels indicates that the method normally used—sanding and washing with acetone—is satisfactory.

ZnO-DMHP-colloidal silica coatings have been exposed for over 300 hours in the Weatherometer with no apparent deterioration.

THE DEVELOPMENT OF HEAT-RESISTANT PAINTS FOR METALS

I. INTRODUCTION

The purpose of this project is to develop protective coatings for metals that can be bonded without heating and that will withstand high temperatures. The coatings must protect the metal substrate at high temperatures that may be developed in flight at high speeds and must also provide protection against normal atmospheric corrosion and erosion.

The present contract provides for continuation of the work carried out for the Bureau of Weapons under previous contracts NO-as-60-6075-c and N0W-61-0546-d.

In studies conducted under the earlier contracts, combinations of a large number of metal oxides and ceramic frits with various liquid organophosphorus compounds were investigated for making coatings with the desired characteristics. Coatings were made on aluminum with mixtures of zinc oxide, dimethyl hydrogen phosphite (DMHP), and ethyl acid phosphate (EAP) that were well bonded to the substrate, and that were resistant to wet abrasion, to heating at 1000°F for over 200 hours, and to thermal shock due to heating to 1000°F and quenching in cold water. However, coatings with these properties could not be produced consistently. Studies of reaction mechanisms for forming these coatings and of the effects on coating properties of additives and of variations in methods of preparing and applying the coating mixtures, in curing conditions, in the components, and in component ratios have been resumed under the current contract.

II. SUMMARY

Several reactions of zinc oxide with polyphosphoric acid, with the methyl and ethyl esters of polyphosphoric acid, and with di-*n*-butylamine phosphate have been studied in attempts to obtain clues to the mechanism of the zinc oxide-DMHP reaction. The products of reactions of zinc oxide with polyphosphoric acid did not form coatings, but they were insoluble in water and relatively heat stable at 1000°F. Coatings prepared from the reaction of zinc oxide with the methyl and ethyl esters of polyphosphoric acid were not water resistant, but some were heat resistant and well bonded. The reaction of di-*n*-butylamine phosphate and zinc oxide produced some coatings that were heat resistant but none were water resistant. The effect of various curing conditions on the properties of these coatings will be studied to determine whether temperature and relative humidity during curing affect the properties of the coatings in a manner similar to their effect on the ZnO-DMHP coatings. If the effects are similar, it may help us to understand the mechanism of the ZnO-DMHP reactions that develop desirable properties and may suggest methods for developing improved coatings.

Studies have been continued to determine the effects of curing environment, time, and condition of substrate on the properties of ZnO-DMHP coatings. A coating that is heat resistant and water resistant has been prepared repeatedly from a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of a colloidal silica dispersion (Ludox LS) by curing at 72°F and 75% RH. Similar coatings cured at other temperatures and relative humidities were either not heat resistant or not water resistant. Studies of other coating compositions that were basically 10 parts of ZnO, 12 parts of DMHP, and 1 part of EAP showed that coatings were either water resistant or heat resistant depending on the relative humidity. But, both properties could not be obtained simultaneously and reproducibly by curing under any of the conditions of temperature and relative humidity that have been tried, and further work along this line is not warranted. However, the role of the colloidal silica in forming satisfactory coatings will be investigated further. The silica may simply be a convenient tool for controlling the moisture in the coating during curing.

A ZnO-DMHP-Ludox LS coating reached a stable weight about 2 hours after it was applied to an aluminum panel. Some preliminary studies indicate that 2 hours is also the minimum time required for curing coatings at 72°F and 75% RH to produce the desired properties. This relationship will be investigated more fully.

Sanding aluminum panels and rinsing them with acetone has been shown to be sufficient pretreatment of panels for the production of good coatings. This is the pretreatment procedure that has been used in all of the recent work.

Heat-resistant, water-resistant coatings prepared from a ZnO-DMHP-Ludox mixture were exposed in an Atlas WeatherOmeter for over 300 hours with no apparent deterioration of the coating. Coatings prepared from a ZnO-DMHP-EAP mixture which were not water resistant tended to become powdery and rub off the panels easily after exposure in the WeatherOmeter. The experiment is being continued.

III. MATERIALS AND PROCEDURES

A. Materials

The organophosphorus compounds used during this report period were commercial-grade products that were obtained from the Virginia Carolina Chemical Corporation. Ludox LS, an aqueous dispersion containing 33% of colloidal silica, was obtained from DuPont de Nemours and Company. The other chemicals used were reagent-grade products that were obtained from General Chemical Division of Allied Chemical Corporation. The aluminum for the coating substrate was Alclad 2024-T3. These are the same grades of materials that have been used in the previous studies.

B. Coating Evaluation Procedures

After application to the aluminum substrate and curing, the coatings were evaluated for appearance, hardness, bonding, water resistance, and heat resistance. Hardness was determined by scratching a coating with a fingernail. Bonding was evaluated by bending a coated panel over a conical mandrel (maximum diameter of bend -0.5 in.), and observing the loss of adhesion of a coating at the bend. Water resistance was determined by rubbing a wet coating with a wet paper towel and observing any loss of adhesion to the panel. Heat resistance was determined by placing a coated panel (coated side up) on a laboratory hot plate at 1000°F for 5 minutes, and then quenching it in cold water and observing the effect on the coating.

A rating system similar to the one outlined in the final report on Contract NO-as-60-6075-c (February 3, 1961) was used to indicate the performance of coatings. In this system, numbers from 1 to 4 are used to indicate the performance of coatings as follows:

Hardness

Rating 1 - very hard, cannot be scratched by a fingernail

Rating 2 - hard, can be scratched by a fingernail if moderate pressure is applied

Rating 3 - soft, can be easily scratched by a fingernail

Rating 4 - very soft, can be rubbed off panel with finger

Surface appearance of coating after curing at room temperature

Rating 1 - smooth, even surface

Rating 2 - rough, uneven surface

Bonding

Rating 1 - good bonding, no loss of coating on bending panel over a 0.5-in. diameter mandrel

Rating 2 - fair bonding, very slight damage at unprotected edges of panel on bending over a 0.5-in. diameter mandrel

Rating 3 - poor bonding, considerable loss of coating on bending panel over a 0.5-in. diameter mandrel

Water resistance (wet abrasion method)

Rating 1 - insoluble and tightly adhered to panel

Rating 2 - insoluble but only partially adhered to panel

Rating 3 - soluble, not adhered to panel

Heat resistance-1000°F for 5 minutes plus quenching

Rating 1 - not damaged

Rating 2 - very slightly damaged at unprotected edges

Rating 3 - badly damaged, coating flaked off or foamed.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

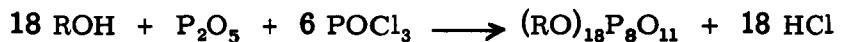
A. Studies of Reactions of ZnO with Phosphates

1. Reaction of zinc oxide with polyphosphoric acid or polyphosphoric esters

The reactions of zinc oxide with polyphosphoric acid and esters of polyphosphoric acid are being studied with the expectation that knowledge of these reactions and the products formed will shed some light on the nature of the reaction occurring in the ZnO-DMHP-EAP mixtures and on the structure of the products of the reaction.

a. Preparation of esters

The preparation of polyphosphoric acid was described in Report 1. The methyl and ethyl esters of polyphosphoric acid were prepared by the method described in U.S. Patent 2,510,033. The reaction involved is represented schematically below:



R = alkyl groups containing 2-18 carbon atoms.

The patent does not mention the preparation of the methyl ester; however, the same reaction techniques were used with methyl alcohol as one of the reactants.

The alcohol was added dropwise to a slurry of phosphoric anhydride and dry heptane which was cooled with an ice bath. After all the alcohol was added, the addition of phosphoryl chloride was started, and, simultaneously, a water aspirator pump was used to evacuate the hydrogen chloride gas formed by the reaction. The reaction mixture was stirred continuously, and the temperature was maintained below 40°C. The evolution of gas (HCl) continued for several hours after addition of the phosphoryl chloride was

complete, indicating continued reaction. Stirring of the reaction mixture under reduced pressure was continued for several hours after evolution of gas had stopped. Finally, the unreacted alcohol and phosphoryl chloride were removed by distillation under reduced pressure.

b. Reactions with polyphosphoric acid

During the previous report period, mixtures of zinc oxide and polyphosphoric acid in various proportions were applied to aluminum panels in attempts to prepare coatings; but only hard, discreet agglomerates, which had no cohesive strength, were formed. Although coatings were not formed, it was of interest to determine whether the reaction product was similar in heat stability and water solubility to the products formed by the ZnO-DMHP-EAP reaction.

A 1-g sample of the material obtained from the reaction of 10 g of zinc oxide and 10 g of polyphosphoric acid was ground to a fine powder and immersed in approximately 200 ml of water at 60°C for 1 hour. The undissolved portion was filtered off and dried. It was found that 93% of the material was insoluble in water. Some coatings prepared by the ZnO-DMHP-EAP reaction that have been rated as water resistant have contained as little as 83% insoluble material. Heating the ZnO-polyphosphoric acid reaction product at 1000°F for 5 minutes caused a weight loss of 9.3%. This is only slightly more than the usual 3-6% loss that occurs when ZnO-DMHP-EAP coatings that are considered heat stable are similarly heated. Thus, the products produced by the reaction of ZnO with polyphosphoric acid are similar to those produced by the ZnO-DMHP-EAP reaction in thermal stability and water resistance, but not in cohesive properties.

c. Reactions with esters of polyphosphoric acid

To further explore the possibility that a polyphosphate is an intermediate in the formation of coatings by the ZnO-DMHP-EAP reaction, the reactions of zinc oxide with the methyl and ethyl esters of polyphosphoric acid are being studied. Preliminary results show that well-bonded, heat-resistant coatings can be prepared by this reaction.

The best coating prepared thus far was formed by reacting 10 parts of ZnO and 6 parts of the methyl ester of polyphosphoric acid, which was barely enough to wet the zinc oxide, and then diluting the reaction product with 6 parts of water and 4 parts of toluene to make a smooth, free-flowing coating mix for application to panels. The reactants were mixed by hand on a glass

plate and doctored onto aluminum panels. The coatings prepared in this manner were smooth, well bonded, and heat resistant, but they were soft and not water resistant. Coatings containing greater proportions of the ester were neither heat resistant nor water resistant.

The coatings that have been studied were cured at laboratory conditions. Similar coatings will be cured under various controlled conditions of temperature and humidity to determine whether more desirable properties can be obtained.

The similarities of properties of the products formed from the reactions of zinc oxide with the polyphosphate esters and with DMHP indicate that formation of a polyphosphate may be one step in the reaction of zinc with DMHP.

2. Reaction of zinc oxide with di-n-butylamine phosphate

U.S. Patent 2,952,562 describes air-curable coatings formed by the reaction of di-n-butylamine phosphate with zinc or lead silicates. Presumably the amine phosphate decomposes slowly to form phosphoric acid and di-n-butylamine, and the phosphoric acid then reacts with the metal silicate to form a coating. It was reasoned that a similar reaction might take place in the case of zinc oxide and DMHP, that is, the DMHP might slowly hydrolyze to an acid that reacts with the zinc oxide. Attempts were made to prepare coatings by the reaction of zinc oxide and di-n-butylamine phosphate to find out whether this reaction produced the same products as the reaction of zinc oxide with DMHP.

A sample of di-n-butylamine phosphate was prepared, as described in the patent, by adding reagent grade phosphoric acid slowly to a solution of di-n-butylamine in isopropyl alcohol and a small amount of water. The resulting solution was clear and had a low viscosity.

In some coating experiments, a smooth, thin layer of zinc oxide was applied to aluminum panels and the di-n-butylamine phosphate solution was sprayed on the zinc oxide. Other aluminum panels were coated by spreading on the panels mixtures of 10 parts of zinc oxide with 12, 20, or 40 parts of the amine phosphate solution. All of the coatings were cured 24 hours at laboratory conditions before evaluation.

All the coatings were soft, but they were well bonded to the aluminum. None of the coatings were water resistant, but the coatings prepared from the mixtures containing 20 or 40 parts of the amine phosphate solution were heat resistant, which makes them of interest for further study.

B. Studies of the ZnO-DMHP Reaction

1. Effects of temperature and relative humidity during curing

The results of previous experiments did not show material differences in the properties of coatings made from mixtures of zinc oxide and DMHP with additions of water, ethyl acid phosphate (EAP), or colloidal silica (Ludox LS) and cured at 100° or 136°F and various humidities. During this report period, similar experiments have been made with curing temperatures of 60°F and 72°F. Coatings containing colloidal silica and cured under the very specific conditions of 72°F and 75% RH were both heat resistant and water resistant. None of the other coatings was both heat and water resistant.

a. ZnO-DMHP-EAP coatings

Coatings were prepared from mixtures that contained 10 parts of zinc oxide, 12 parts of DMHP, and 1 part of EAP. The mixtures were prepared and coated on aluminum panels as described in Report 1. The panels were placed in a controlled environment within 10 minutes after being coated. Data on curing conditions and coating properties are given in Table I.

In earlier studies at 100° and 136°F, a critical relative humidity was found for curing at each temperature. Coatings cured above the critical relative humidities were water resistant but not heat resistant; coatings cured below the critical relative humidities were heat resistant but not water resistant. No such critical relative humidity was found for curing ZnO-DMHP-EAP coatings at 60° or 72°F.

Coatings cured at 72°F and 65%, or less, RH were heat resistant but not water resistant.(Table I). Erratic results were obtained on coatings cured at 75% RH. In one trial, the coating was heat resistant; in another trial, the coating was water resistant; and, in a third trial, the coating was neither heat resistant nor water resistant. The coatings cured at 72°F and 80% RH were neither heat nor water resistant. No explanation for this behavior is known.

Table I. Effect of Curing Conditions on Properties of Coatings

Coating composition, parts by weight ^a	Curing conditions				Rating of coatings cured 1 day			
	ZnO	DMHP	EAP	Water	Relative humidity, %	Temperature, °F	Water resistance	Heat resistance
10	12	1	-	-	90	60	3	1
10	12	1	-	-	99	60	3	1
10	12	1	1	-	35	72	3	1
10	12	1	1	-	60	72	3	1
10	12	1	1	-	65	72	3	1
10	12	1	1	-	75	72	3	2
10	12	1	1	-	75	72	3	1
10	12	1	1	-	75	72	3	1
10	12	1	1	-	80	72	3	2
10	12	1	1	-	80	72	3	3
10	12	1	1	1	35	72	3	1
10	12	1	1	1	35	72	3	1
10	12	1	1	1	60	72	3	1
10	12	1	1	1	65	72	3	1
10	12	1	1	1	65	72	3	2
10	12	1	1	1	65	72	3	3
10	12	1	1	1	65	72	2	1
10	12	1	1	1	65	72	3	1
10	12	1	1	1	75	72	3	2
10	12	1	1	1	75	72	2	1
10	12	1	1	1	75	72	1	2
10	12	1	1	1	75	72	3	1
10	12	1	1	1	75	72	2	2
10	12	1	1	1	75	72	3	3
10	12	1	1	1	80	72	3	3
10	12	1	1	1	80	72	3	3

DMHP = dimethyl hydrogen phosphate; EAP = ethyl acid phosphate.

Coatings prepared from the mixture described above and containing 1 or 4 parts of water were also cured at the various temperatures and relative humidities. No differences were found in the properties of these coatings cured at 136° or 100°F and the coatings that did not contain water. At a curing temperature of 72°F, the only difference noted was that erratic results were obtained at 65% RH; however, the data are not conclusive.

The ZnO-DMHP-EAP coatings cured at 60°F and 90 or 99% RH were usually heat resistant but not water resistant. Some representative data showing these results are also given in Table I.

These data combined with those previously reported (Report 1) indicate a general correlation between the relative humidity and temperature for curing and the properties developed in ZnO-DMHP-EAP coatings. As the curing temperature is increased, the permissible maximum relative humidity for obtaining heat resistance is decreased from about 100% at 60°F to 38% at 136°F. The production of water resistance in the coatings also appears to follow a trend, but, to obtain water resistance, curing should be carried out above certain values of relative humidity that decrease with increasing temperature.

The opposing humidity requirements for obtaining both water and heat resistance probably explain why it has been so difficult to obtain both properties in a single coating. Presumably, the coatings that have shown excellent stability to both heat and water were prepared under chance combinations of conditions that were favorable.

Although the data obtained show that temperature and relative humidity play a part in determining coating properties, it appears that no relatively broad band of curing temperature and relative humidity exists where satisfactory coatings can be made. Because little would be gained by further work along this line, no further experiments of this type are planned. Work in the future will be concentrated on determining the role of water in the development of specific properties in coatings formed by the reactions of zinc oxide with phosphorus compounds.

b. ZnO-DMHP-Ludox coatings

Earlier studies under Contract NOw-61-0546-d yielded promising results with ZnO-DMHP coatings containing colloidal silica that made these mixtures of interest for further study. In resuming the study of this composition, coatings on aluminum panels were prepared from a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS (an aqueous dispersion of colloidal silica containing 33% solids) and cured at 60°, 72°, 100°, and 136°F and various relative humidities. The properties of the coatings are shown in Table II.

Coatings cured at 136° and 100°F: Coatings that were cured at 136°F and above a relative humidity of about 40% were water resistant but not heat resistant, while coatings cured at a lower relative humidity were heat resistant but not water resistant. A similar relationship was found for curing at 100°F; at this temperature the critical humidity was about 56%.

Coatings cured at 72°F: A different curing pattern was observed for ZnO-DMHP-Ludox coatings cured at 72°F. Coatings cured at 65% relative humidity or below were neither heat resistant nor water resistant; coatings cured at 75% relative humidity were both heat resistant and water resistant; and coatings cured at 80% relative humidity were water resistant but not heat resistant. The ability to produce coatings that were both heat and water resistant by curing at 72°F and 75% relative humidity was checked repeatedly. Thus far, in twelve different trials in which the ZnO-DMHP-Ludox coatings were cured at 72°F and 75% relative humidity, ten coatings were both heat resistant and water resistant and the other two were water resistant and had marginal heat resistance.

Coatings cured at 60°F: Coatings of this type that were cured at 60°F and at relative humidities of 90 to 99% were heat resistant but not water resistant.

These results show that the curing conditions that give a coating that is both water resistant and heat resistant are apparently quite specific. Attempts will be made to more clearly define the role Ludox plays in the formation of heat-resistant and water-resistant coatings. Coatings will be prepared in which materials similar to Ludox will be substituted for it. These will include materials such as Baymal (boehmite), Cab-O-Sil (silica), and Hi-Sil 233 (precipitated hydrated silica).

Table II. Properties of ZnO-DMHP-Ludox Coatings Cured Under Various Conditions^a

Relative humidity, %	Curing conditions	Temperature, °F	Ratings of coatings cured 24 hours		
			Hardness	Bonding	Water resistance
90		60	1	1	3
99		60	3	3	3
35		72	3	1	3
60		72	1	2	3
65		72	1	1	3
75		72	1	1	1
80		72	1	1	1
20		100	1	1	3
55		100	1	1	3
57		100	1	2	1
38		136	3	1	3
43		136	1	2	1
49		136	1	3	1

^a Coatings prepared from a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS.

2. Effects of curing time

The weight loss of a ZnO-DMHP-Ludox coating during curing was followed to determine how the rate of weight loss varied with time and how long is required for a coating to reach weight equilibrium.

a. Weight loss during curing

A coating mixture was prepared from 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS. The mix was coated on a preweighed aluminum panel within 2 minutes after mixing, and the coated panel was placed on an analytical balance so the weight loss could be followed during curing. All of these operations were carried out in air at 72°F and 60% RH.

Figure 1 shows a curve of coating weight versus time. No significant fluctuations occurred in the rate of weight loss during drying to indicate a step-wise reaction. The weight of the coating reached a constant value in approximately 90 minutes.

Theoretically, assuming complete hydrolysis of the DMHP to methanol and making allowance for the water added in the Ludox, there could be a maximum of about 35% volatiles as methanol and water. The weight lost by the coating in the reaction carried out on the analytical balance was approximately 37%. This would indicate that the DMHP is quantitatively hydrolyzed.

Further experiments will be carried out at 72°F and at relative humidities of 75% and higher to determine whether the weight loss curves are similar when coatings are cured under conditions which produce heat-resistant, water-resistant coatings and coatings which are only water resistant. The weight loss curve of the coating cured at 72°F and 60% RH represents that for a coating which is heat resistant but not water resistant.

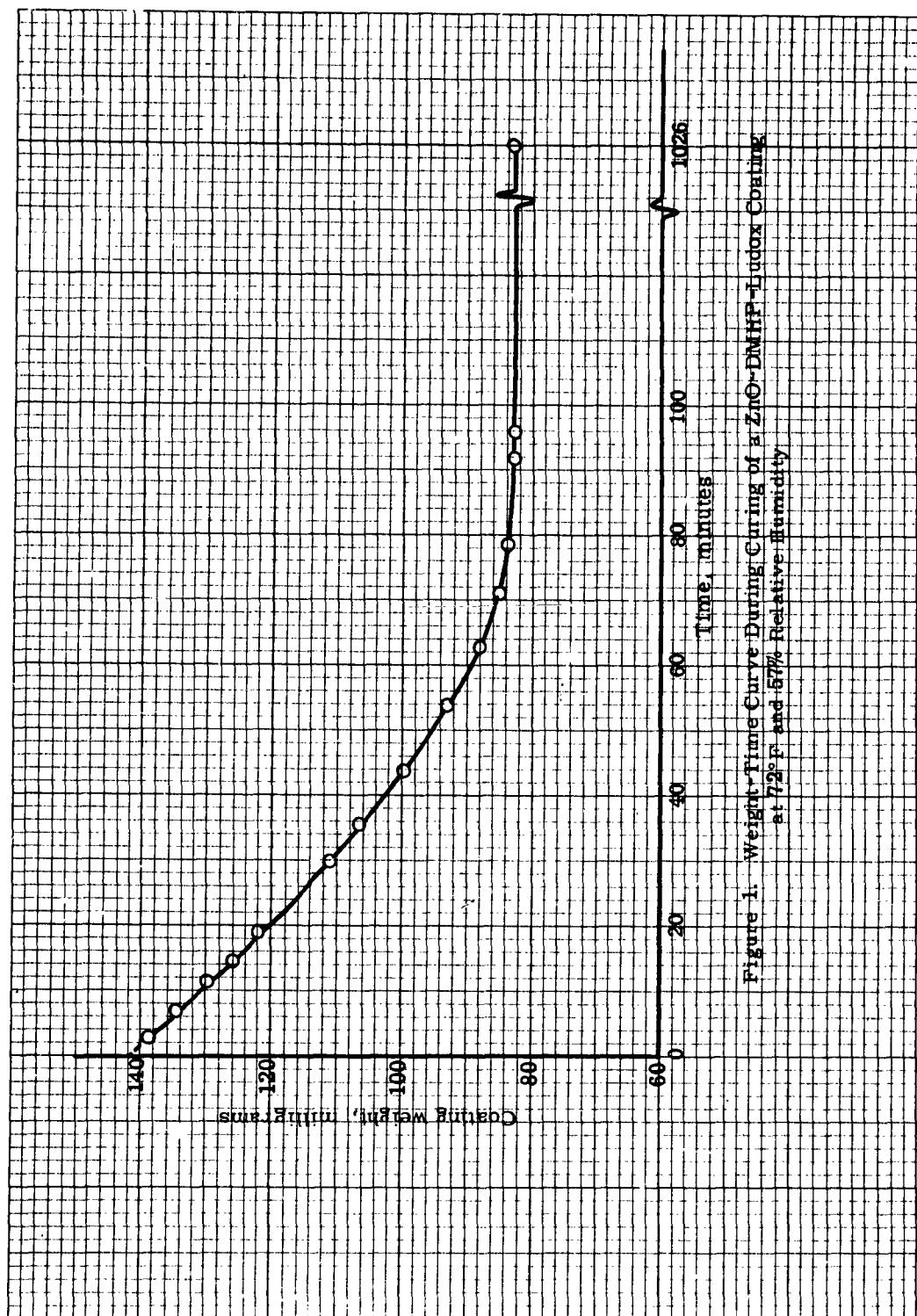


Figure 1. Weight-TIME Curve during curing of a ZnO-DMHP-Tudor Coating at 72°F and 67% Relative Humidity.

b. Curing time at 72°F and 75% RH

It is of interest to determine whether the time required for a coating to reach weight stability correlates with the time required for a coating to be cured under controlled conditions to obtain desired properties on complete curing. Preliminary data obtained indicate that the time required for a coating to cure at 72°F and 75% relative humidity to obtain heat-resistant, water-resistant coatings is between 1 and 2 hours. Further experiments are to be made in which several panels of a coating containing 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS will be prepared and cured for various times at 72°F and 75% relative humidity.

3. Condition of substrate

It is known that the condition of the substrate often affects the properties of coatings. A study was undertaken to determine what effects various methods of preparing the aluminum panels (Alclad 2024-T3) had on the properties of cured coatings. Panels were prepared for coating in the following ways:

Panels were merely washed with acetone to remove grease.

Panels were sanded lightly to remove any oxide from the surface and then washed with acetone. This is the method that has generally been used. It produces a rougher surface than the other methods which should improve the adhesion of coatings.

Panels were soaked in DMHP. In the preceding report, experiments were described in which heat-resistant, water-resistant coatings were dissolved in DMHP and recoated on panels. Removal of the hard crust formed by heating the coated panels exposed a panel surface which had obviously been modified. This exposed surface was not affected by heating to 1000°F, or by wet or dry abrasion. Subsequent investigation during this report period determined that a similar surface could be produced by soaking an aluminum panel in DMHP for periods of 8 hours or longer. It is known that pretreating of substrates will often result in better bonding of coatings; therefore, panels were pretreated in this manner for coating studies.

Panels were ground from 0.032-in. to 0.025-in. thickness and washed with acetone. The aluminum panels used in this study consisted of a core aluminum alloy overcoated with a second aluminum alloy. The overcoated alloy was removed to determine if different properties were obtained in coatings on the core alloy.

Panels were ground from 0.032 in. to 0.025 in. and wire-brushed to obtain a rough surface.

The panels prepared in these various ways were coated with a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox and cured at 72°F and 75% RH. The properties of the coatings on the various panels are listed in Table III. All the coatings were satisfactory except those applied to panels which were merely washed with acetone. These data indicate that sanding the panels and washing them with acetone is sufficient preparation for coating. This has been our practice in our past work and it will be continued.

Table III. Properties of ZnO-DMHP-Ludox Coatings on Panels Treated in Various Ways

Treatment of panel ^b	Properties of coatings ^a					Heat Resistance
	Hardness	Surface	Bonding	Water Resistance		
Washed	2	1	3	3	3	3
Sanded and washed	1	1	1	1	1	1
Soaked in DMHP	1	1	1	1	1	1
Ground and washed	1	1	1	1	1	1
Ground, wire-brushed and washed	1	1	1	1	1	1

^a Coatings prepared from 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox.

^b All washes were with acetone.

C. Studies of the Weatherability of ZnO-DMHP-EAP Coating

Two sets of coated aluminum panels are being exposed to light and water spray in an Atlas WeatherOmeter. For one set, a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS was coated on aluminum panels and cured at 72°F and 75% RH for 24 hours. The coatings were water resistant, heat resistant, and well bonded. For the other set, coatings were made with a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of EAP and cured at 72°F and 75% RH for 24 hours. Coatings on this set of panels were not water resistant.

The cured coatings of both types were placed in the WeatherOmeter operating at approximately 100°F with cyclic water spray. After exposure for over 300 hours, the coatings containing Ludox appear to be essentially unchanged; however, the coatings made with EAP are powdery and easily rubbed off the panels. Exposure of the panels will be continued.

V. FUTURE WORK

The study of the chemical nature of the ZnO-phosphate coatings will be continued. The reactions of polyphosphate esters and di-*n*-butylamine phosphate with zinc oxide will be studied further. It is expected that it will be learned whether phosphate intermediates such as these are formed in the ZnO-DMHP reaction.

The effects of humidity during curing in determining the properties of coatings may be related to the oxidation of phosphites to phosphates, and an effort will be made to determine whether oxidation is a factor. Coatings formed with di-*n*-butylamine phosphate will be compared with coatings formed with di-*n*-butylamine phosphate. The effect of oxidation inhibitors and accelerators on ZnO-DMHP coatings also will be evaluated. The effect of substrate on oxidation will be investigated by coating stainless steel panels, and comparing the properties of the coatings with the properties of the same coatings on aluminum panels.

During past report periods, we have found and reported that at times coatings were formed that were not water resistant initially, but that they were water resistant after being heated to 1000°F for 5 minutes. It is obvious that some change in coating make-up is occurring during heating. Accordingly, modified thermogravimetric analyses and differential thermal analyses will be run on coatings to see whether the change in coating results in a weight loss or weight gain and whether this loss or gain is associated with

an exothermic or endothermic reaction. Also, it may be possible to determine the temperatures at which changes take place. These data may give indications of the kind of reaction that takes place to form water-resistant coatings.

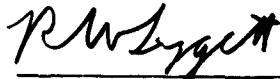
Analytical data on the compositions of the portions of coatings that are water soluble and the portions that are insoluble in both heat-resistant, non-water-resistant coatings and in water-resistant, nonheat-resistant coatings are being obtained. An attempt will be made to correlate differences in compositions with difference in the properties of the coatings.

In attempts to more clearly define the role of colloidal silica in satisfactory coatings, several similar materials will be evaluated in coatings. These will include materials such as Cab-O-Sil, Hi-Sil 233, and Baymal.

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